

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 June 2001 (14.06.2001)

PCT

(10) International Publication Number
WO 01/42165 A2

(51) International Patent Classification⁷: C04B 40/00

(21) International Application Number: PCT/EP00/12216

(22) International Filing Date: 1 December 2000 (01.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9928977.9 8 December 1999 (08.12.1999) GB

(71) Applicant (for all designated States except US): MBT
HOLDING AG [CH/CH]; Vulkanstrasse 110, CH-8048
Zürich (CH).

(72) Inventor; and

(75) Inventor/Applicant (for US only): HOFMANN, Thomas
[CH/CH]; Dorfstrasse 22, CH-8166 Niederweningen (CH).

(74) Agent: MCSTEA, John, Anthony; MBT (Schweiz) AG,
Patents and Trade Marks, Vulkanstrasse 110, CH-8048
Zürich (CH).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— Without international search report and to be republished
upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF CONCRETE ACCELERATOR

(57) Abstract: An alkali-free accelerator for sprayed concrete is prepared by dissolving aluminium sulphate in water and amorphous aluminium hydroxide in water optionally containing amine, and optionally adding at least one stabiliser, selected from hydroxycarboxylic acids and phosphoric acids and non-alkaline salts thereof, and at least one defoaming agent.

WO 01/42165 A2

Preparation of concrete accelerator

This invention relates to cementitious compositions and to accelerators for use therein, particularly for sprayed concrete.

5

The application of concrete to a substrate by spraying from a nozzle (commonly referred to as "shotcreting") is a well-established technology, and is widely used in such applications as the lining of tunnels. It is important that the sprayed concrete set very rapidly on the substrate, and this is achieved by the addition to the concrete at the nozzle
10 of an accelerator. These accelerators are quite different from those used with conventional concrete and have traditionally included such materials as alkali metal hydroxides, aluminates and silicates.

The highly alkaline nature of these materials has given handling problems. It also
15 means that their use in confined spaces such as tunnels has led to very unpleasant working atmospheres. Recent attempts to avoid such materials have involved the use of aluminium compounds and typical examples may be found in European Patents 0 076 927, 0 775 097 and 0 742 179, Australian Patent 706917 and European Applications 0 812 812 and 0 946 451.

20

It has now been found that it is possible to prepare an accelerator for sprayed concrete by a simple process, which accelerator performs especially well. The invention therefore provides a method of preparing an accelerator for sprayed concrete consisting essentially of the steps of

25

- (i) dissolving aluminium sulphate and aluminium hydroxide in water which optionally contains at least one amine dissolved therein, to give a clear solution; and
- 30 (ii) optionally adding at least one of at least one stabiliser and at least one defoaming agent;

the proportions of ingredients present being such that the final product contains from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by weight of amorphous aluminium hydroxide, up to 15% by weight amine, up to 3% by weight defoaming agent and up to 0.06 mol/kg. stabiliser, the stabiliser being selected
5 from hydroxycarboxylic acids, phosphoric acids and non-alkaline salts of phosphoric acids.

The invention additionally provides an accelerator for use with sprayed concrete prepared by such a method.

10

The aluminium sulphate used may be any commercially-available material. Aluminium sulphates differ in their purity and constitution, the most common being so-called "17%" because it contains 17% of Al_2O_3 . In practical terms, the weight percentage of 17% aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3 \text{ H}_2\text{O}$, which should be used in the process
15 according to the invention lies in the range of from 30% to 60%, preferably from 40%-48%.

The aluminium hydroxide may be any commercially-available amorphous aluminium hydroxide. Although all such aluminium hydroxides will give satisfactory
20 results, it is generally true that the more recent the date of manufacture, the better the result. In addition, aluminium hydroxides which, as a result of their particular manner of manufacture, contain a small proportion of aluminium carbonate (up to 5%) are easier to dissolve and are preferred materials. This behaviour is not obtained by simply adding aluminium carbonate to pure aluminium hydroxide. Although very small quantities of
25 aluminium hydroxide may be used (less than 0.1% is possible), a significant improvement is observed at 5% or more. The preferred range of weight proportions is from 8-25%, preferably from 15-25%.

Although aluminium sulphate, aluminium hydroxide and water can, when utilised
30 together in the process of the invention, give accelerators with good properties, the properties can be considerably enhanced by the use of one or more of three optional, but preferred, components.

The first of these is amine. This must be water-soluble, otherwise there is no restriction on the choice of amine. Preferred amines are alkanolamines, such as diglycolamine, diethanolamine and triethanolamine, diethanolamine being particularly preferred. Up to 10% by weight amine may be used, preferably from 4-7%.

The second preferred additional component is stabiliser, which may be added at the end of the process. This is a material which prevents the aluminium hydroxide/aluminium sulphate solution either from precipitating or from forming a gel. Without stabiliser, the solution will function well as an accelerator, but it will often lack stability and therefore shelf life, necessitating its use very shortly after manufacture, something usually not practical. It is possible and permissible to use more than one stabiliser.

The stabilisers for use in this invention are hydroxycarboxylic acids, phosphoric acids and non-alkaline salts of phosphoric acids. The hydroxycarboxylic acid may be selected from any such acid known to the art. The preferred acid is citric acid, but many other acids, such as lactic acid and ascorbic acid may also be used.

By "phosphoric acid" is meant one of the acids orthophosphoric acid (H_3PO_4), metaphosphoric acid ($(\text{HPO}_3)_x$) and pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$). By "non-alkaline salts" is meant salts which do not include the alkali metals sodium and potassium. Thus, for example, lithium, calcium and magnesium phosphate salts may be used.

The third preferred additional component, defoaming agent, may be any such material known to the art. Most of these are proprietary commercial materials whose precise composition is never revealed, but any such material known to the art is suitable. Typical examples include silicone types such as AGITAN (trade mark) and fatty acid polyether types such as LUMITEN (trade mark) EL.

The defoaming agent may be used at a rate out up to 5% (solids by weight of the whole composition), preferably from 0.5%-3%. The use of defoaming agent makes the use of less fresh aluminium hydroxides easier. It is believed, without restricting the scope of

the invention in any way, that its presence helps in the removal of carbon dioxide which accumulates on the surface of the aluminium hydroxide over time. Surprisingly, provided that the defoamer contains no silicone and that it is not present to the extent of more than 3%, it gives an appreciable improvement in setting time over that of an identical
5 composition without defoaming agent or with silicone types.

The process of the invention is readily carried out with standard equipment, and the skilled person will have no difficulty in doing so. It will be appreciated that in order to achieve solutions at the various stages, some heating may be necessary, typically to about
10 50-60°C.

In the process, the clear solution can be produced by any convenient method. It is possible to add the aluminium sulphate and aluminium hydroxide sequentially in any order to water. It is also possible to add them together to water, or to dissolve or disperse
15 them individually in two different quantities of water and then combine these quantities.

Preferably, the aluminium sulphate and the aluminium hydroxide are added sequentially to water. Preferably the aluminium sulphate is first dissolved in water; aluminium sulphate will dissolve with heating. To this solution the aluminium hydroxide
20 is then added. A clear solution is obtained.

It is possible, although less preferable, first to add the aluminium hydroxide to the water. Aluminium hydroxide does not dissolve readily in water, but gives a fine suspension. To this suspension the aluminium sulphate is added. A clear solution is
25 obtained.

The precise nature of the product of the process is not known. It is certainly not a mere mixture of the original components (the fact that the product is a clear or slightly turbid solution and not an opaque suspension typical of aluminium hydroxide is evidence
30 of this), and without restricting the invention in any way, it is believed to be oligomeric or polymeric in nature.

The accelerator thus prepared gives excellent results when used as a shotcrete accelerator. Shotcrete treated therewith hardens rapidly and has good final strength. The accelerator has a long shelf-life, is resistant to changes in temperature and is completely non-alkaline, thus leading to better working environments.

5

The invention is further illustrated by the following non-limiting examples.

Examples 1-3

Preparation of accelerators according to the invention.

10 The weight proportions used are as follows:

	Example 1	Example 2	Example 3
17% aluminium sulphate	46%	48%	40%
amorphous aluminium hydroxide	18%	18%	18%
15 water	30%	28%	28%
diethanolamine (90% solution)	6%	6%	4%

The diethanolamine is dissolved in the water and the aluminium sulphate is then dissolved in this solution. This is achieved by heating the solution to 50°-60°C and adding
20 with stirring, stirring being continued until a clear solution is obtained. To this heated, stirred solution is gradually added the aluminium hydroxide, and stirring is continued until a clear solution is obtained.

Example 4

25 An accelerator is prepared by the method and using the materials of Examples 1-3, except that the water content is lowered to 28.7% and there is added 1.3% citric acid monohydrate. This is added after the addition of the aluminium hydroxide, the solution being cooled to room temperature prior to addition. The result is a clear solution.

30 Example 5

Testing of accelerators in mortar.

The mortar used for the testing has the following formulation:

	Normo 4 Portland cement	450 parts
	SIA 215-1 standard sand	1350 "
	phosphonic acid-based cement	
5	hydration stabiliser ¹	0.3% by weight of cement
	polycarboxylate superplasticiser ²	0.6% by weight of cement

1. DELVO (registered trade mark) stabiliser ex MBT

2. GLENIUM (registered trade mark) 51 ex MBT

10

Sufficient water is added to give a water/cement (w/c) ratio of 0.47.

To samples of the mortar, each of the accelerators of Examples 1, 2 and 4 is added at a rate of 7% by weight of cement, and the initial and final setting times are measured by
15 the Vicat test procedure of EN 196-3. In addition, a commercially-available alkali-free accelerator MEYCO (trade mark) SA 160 was also tested. The results are as follows.

20		Example 1	Example 2	Example 4	Commercial accelerator
	Initial (min)	4	1	3.5	3
	Final (min)	8	5.5	8.5	6

25

Claims

1. A method of preparing an accelerator for sprayed concrete, consisting essentially of the steps of
 - (i) dissolving aluminium sulphate and aluminium hydroxide in water, optionally containing at least one amine dissolved therein, to give a clear solution; and
 - (ii) optionally adding at least one of at least one stabiliser and at least one defoaming agent;
- the proportions of ingredients present being such that the final product contains from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by weight of amorphous aluminium hydroxide, up to 15% by weight amine, up to 3% by weight defoaming agent and up to 0.06 mol/kg. stabiliser, the stabiliser being selected from hydroxycarboxylic acids, phosphoric acids and non-alkaline salts of phosphoric acids.
2. A method according to claim 1, wherein there is additionally present in the water at least one water-soluble amine.
3. A method according to claim 1 or claim 2, wherein there is added at least one of an at least one stabiliser and at least one defoaming agent.
4. A method according to claim 3, wherein there is added at least one stabiliser.
5. A method according to claim 3, wherein there is added at least one defoaming agent.
6. A method according to claim 5, wherein the defoaming agent contains no silicone and is present to a maximum extent of 3%.

7. A method according to any one of claims 1-6, wherein the stabiliser is at least one hydroxycarboxylic acid.

5 8. A method according to claim 1, wherein the clear solution is prepared by the steps of

(i) dissolving aluminium sulphate in water, optionally containing at least one amine dissolved therein; and

10 (iii) dissolving amorphous aluminium hydroxide in the solution of (i) until a clear solution is obtained.

9. A method according to claim 8, wherein there is added to the clear solution at least one of (a) at least one defoaming agent, and (b) at least one stabiliser selected from
15 hydroxycarboxylic acids, phosphoric acids and non-alkaline salts of phosphoric acids, preferably from hydroxycarboxylic acids.

10. An accelerator for use with sprayed concrete, prepared by a process according to any one of claims 1-9.

20

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 June 2001 (14.06.2001)

PCT

(10) International Publication Number
WO 01/42165 A3

(51) International Patent Classification⁷: **C04B 22/14**,
103/10

(21) International Application Number: PCT/EP00/12216

(22) International Filing Date: 1 December 2000 (01.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9928977.9 8 December 1999 (08.12.1999) GB

(71) Applicant (*for all designated States except US*): **MBT HOLDING AG** [CH/CH]; Vulkanstrasse 110, CH-8048 Zürich (CH).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **HOFMANN, Thomas** [CH/CH]; Dorfstrasse 22, CH-8166 Niederweningen (CH).

(74) Agent: **MCSTEA, John, Anthony**; MBT (Schweiz) AG, Patents and Trade Marks, Vulkanstrasse 110, CH-8048 Zürich (CH).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:
15 November 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF CONCRETE ACCELERATOR

(57) Abstract: An alkali-free accelerator for sprayed concrete is prepared by dissolving aluminium sulphate and amorphous aluminium hydroxide in water which optionally contains one amine, and optionally adding at least one stabiliser, selected from hydroxycarboxylic acids and phosphoric acids and non-alkaline salts thereof, and at least one defoaming agent.

WO 01/42165 A3



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/12216

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B22/14 //C04B103/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 78688 A (HOFMANN THOMAS ;MBT HOLDING AG (CH)) 28 December 2000 (2000-12-28) claims	1,2,4,7, 9,10
A	WO 96 05150 A (SANDOZ LTD ;SANDOZ AG (DE); SANDOZ AG (AT); LEIKAUF BERNHARD (CH)) 22 February 1996 (1996-02-22) & EP 0 775 097 A 28 May 1997 (1997-05-28) cited in the application	1,2,4
A	EP 0 812 812 A (MBT HOLDING AG) 17 December 1997 (1997-12-17) cited in the application claims; examples	1,2,4,10
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

4 July 2001

Date of mailing of the international search report

11/07/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Theodoridou, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/12216

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 742 179 A (SIKA AG) 13 November 1996 (1996-11-13) cited in the application page 2, line 39 - line 54 ---	1,8
A	DE 196 25 853 A (SANDOZ AG) 2 January 1997 (1997-01-02) claims ---	1,2,4,7, 9,10
A	WO 95 25702 A (RHONE POULENC CHIMIE ;BOUYGUES SA (FR); BERTONCINI ANDRE (CH); DUG) 28 September 1995 (1995-09-28) claims -----	1,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/12216

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0078688	A	28-12-2000	NO 20010774 A	15-02-2001
WO 9605150	A	22-02-1996	AT 174887 T	15-01-1999
			AU 701619 B	04-02-1999
			AU 3257895 A	07-03-1996
			DE 69506881 D	04-02-1999
			DE 69506881 T	02-06-1999
			EP 0775097 A	28-05-1997
			ES 2125644 T	01-03-1999
			FI 970551 A	07-02-1997
			JP 10504273 T	28-04-1998
			US 5968256 A	19-10-1999
EP 0812812	A	17-12-1997	AU 723970 B	07-09-2000
			AU 2369697 A	18-12-1997
			BR 9703581 A	22-09-1998
			CN 1171378 A	28-01-1998
			JP 10087358 A	07-04-1998
			NO 972740 A	15-12-1997
			US 5935318 A	10-08-1999
EP 0742179	A	13-11-1996	AT 185540 T	15-10-1999
			DE 59603322 D	18-11-1999
			DK 742179 T	10-04-2000
			ES 2139272 T	01-02-2000
			GR 3032188 T	27-04-2000
			NO 961799 A	11-11-1996
			TR 960992 A	21-11-1996
DE 19625853	A	02-01-1997	AT 402920 B	25-09-1997
			AT 113896 A	15-02-1997
			AU 706917 B	01-07-1999
			AU 5617796 A	09-01-1997
			CH 691123 A	30-04-2001
			ES 2121689 A	01-12-1998
			FR 2736046 A	03-01-1997
			GB 2302688 A, B	29-01-1997
			GR 96100216 A	28-02-1997
			IT RM960447 A	29-12-1997
			JP 9012350 A	14-01-1997
			US 5997630 A	07-12-1999
WO 9525702	A	28-09-1995	FR 2717416 A	22-09-1995
			AU 1953795 A	09-10-1995

THIS PAGE BLANK (USPTO)